Research Article

Multicomponent Reactions, Solvent-Free Synthesis of 2-Amino-4-aryl-6-substituted Pyridine-3,5-dicarbonitrile Derivatives, and Corrosion Inhibitors Evaluation

Naglaa F. H. Mahmoud and Ahmed El-Sewedy

Department of Chemistry, Faculty of Science, Ain Shams University, Abbasia, 11566 Cairo, Egypt

Correspondence should be addressed to Naglaa F. H. Mahmoud; naglaa.fawzy@yahoo.com

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A number of 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitrile derivatives were synthesized via one-pot multicomponent condensation reactions of different aromatic aldehydes with malononitrile and different primary amines, using different molecular ratios and different reaction conditions to achieve considerable product yields. Moreover, we succeeded, for the first time to develop a new method to synthesize the aforementioned under the fusion condition without using solvent and catalysts. With this method, a wide range of novel 2-amino-3,5-dicyano-4-aryl-6-substituted aminopyridine derivatives were synthesized with high yields and broad substrate of functional groups. The synthesized pyridine derivatives were found to have a corrosion inhibition efficiency, the rate of which increased with the increasing concentration of the derivatives. The structures of the new compounds were elucidated by spectroscopic data and elemental analyses.

1. Introduction

Multicomponent reactions (MCRs) have drawn high efforts in recent years owing to exceptional synthetic efficiency, high selectivity, and procedural simplicity [1–6]. One-pot multicomponent reactions are a new method to construct heterocyclic compounds with bond making and/or bond breaking in one step with high atom economy, and the diversity can be achieved by varying the reacting components. A large number of organic reactions which were carried out afforded higher yields, shorter reaction time, and milder conditions [7–9].

Substituted pyridines were used as medical scaffolds because they are part of many natural product structures [10, 11]. Pyridine derivatives have also showed a broad spectrum of biological activities such as antimitotic agents [12], anti-inflammatory substances [13], and anticonvulsants [14]. In addition, they also regulate arterial pressure [15] and cholesterol level in blood [16]. Furthermore, they were utilized as electrical materials [17] and chelating agents [18].

Furthermore, organic compounds rich in heteroatoms behave as corrosion inhibitors, when they are absorbed in the metal surface to form a protective layer preventing cathodic and/or anodic reactions and forming a compact barrier film [19–21].

From the synthetic aspect, most of the existing studies on 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitrile derivatives [22] were synthesized by ZnCl_2 -catalyzed multistep methods [23] and one-pot multicomponent reactions [24] with good yield.

The addition of corrosion inhibitors is a useful approach to protect mild steel (MS) surfaces from corrosion damage [25]. Considerable efforts are made to synthesize new organic molecules offering various molecular structures. The most synthesized compounds are the nitrogen-heterocyclic compounds which are known to be excellent complex or chelate-forming substances with metals of transition series [26]. Also, the heterocyclic compounds containing nitrogen atoms can be easily protonated in the acidic medium to exhibit good inhibitory action [27].

In our preliminary studies, we have investigated the one-pot multicomponent reactions of different aromatic aldehydes with malononitrile and primary amines, using various Lewis acids such as ZnCl_2 , AlCl_3 , and FeCl_3 in ethanol as a solvent with different molecular ratios. The pyridine derivatives were obtained in good yield using solvent and catalyst-free condition under the fusion condition. Aminopyridine derivatives and their corrosion inhibition properties were evaluated by weight loss measurements of steel with different concentrations of inhibitors.

2. Results and Discussion

2.1. Chemistry. According to literature [22], 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitrile derivatives were synthesized by a multistep pathway in the presence of ZnCl_2 only as the catalyst at 75°C with 81% yield.

In our present study, we have investigated the one-pot multicomponent reactions (MCRs) to prepare aminopyridine derivatives **1–20** using different Lewis acid catalysts such as ZnCl_2 , AlCl_3 , and FeCl_3 using a molar ratio of 1 : 2 : 3 (aromatic aldehydes: malononitrile: primary amines) where the desired products were obtained in moderate yields.

The first trial was performed using one equivalent of aromatic aldehydes, two equivalents of malononitrile, and one equivalent of primary amines in the presence of ZnO (nano particles), CAN, NaOEt , and/or H_3PO_4 as catalysts in refluxing ethanol for 12 h, and no products were observed even after changing the molar ratio of amines to two equivalents and/or three equivalents (Table 1, entries 1–12) (Scheme 1).

The second trial was carried out using ethanolic solutions of aromatic aldehydes, malononitrile, and primary amines in the presence of Lewis acids as catalysts such as AlCl_3 , ZnCl_2 , and FeCl_3 . The reaction mixture was refluxed for 6 h using different molar ratios 1 : 2 : 1, 1 : 2 : 2, and 1 : 2 : 3 (aromatic aldehydes: malononitrile: primary amines), respectively. The desired products were obtained with the molar ratios of 1 : 2 : 3 in moderate yields (Table 1, entries 13–21).

As initial endeavor, the reaction was performed with aromatic aldehydes (1 equivalent), malononitrile (2 equivalents), and primary amines (1 equivalent) by fusion, solvent, and catalyst-free condition, and a solid precipitate of different 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitrile derivatives **1–20** were separated out with high yields (Table 1, entry 22) (Scheme 2).

The formation of the desired products **1–20** could be explained via the formation of the arylidene molecule than the Michael addition of malononitrile on the double bond of the arylidene moiety forming the intermediate which underwent cyclization by the nucleophilic attack of amine on the cyanocarbon followed by aromatization to the final products **1–20** (Scheme 3).

As a conclusion, we have developed for the first time a solvent-free, one-pot multicomponent reaction without using any catalysts. With this method, a wide range of novel 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitrile derivatives were synthesized in high yields with a board

TABLE 1: Optimization of reaction conditions.

Entry	Catalyst	Aldehyde	Malononitrile	Amine	Yield (%)	
1	ZnO	1.5	1	2	1	—
2	ZnO	1.5	1	2	2	—
3	ZnO	1.5	1	2	3	—
4	CAN	1.5	1	2	1	—
5	CAN	1.5	1	2	2	—
6	CAN	1.5	1	2	3	—
7	NaOEt	1.5	1	2	1	—
8	NaOEt	1.5	1	2	2	—
9	NaOEt	1.5	1	2	3	—
10	H ₃ PO ₄	1.5	1	2	3	—
11	H ₃ PO ₄	1.5	1	2	3	—
12	H ₃ PO ₄	1.5	1	2	3	—
13	AlCl ₃	1.5	1	2	1	—
14	AlCl ₃	1.5	1	2	2	—
15	AlCl ₃	1.5	1	2	3	25
16	ZnCl ₂	1.5	1	2	1	—
17	ZnCl ₂	1.5	1	2	2	—
18	ZnCl ₂	1.5	1	2	3	45
19	FeCl ₃	1.5	1	2	1	—
20	FeCl ₃	1.5	1	2	2	—
21	FeCl ₃	1.5	1	2	3	37
22	Neat reaction	0	1	2	1	90

CAN = ceric ammonium nitrate.

substrate of functional groups. Those derivatives are depicted in Scheme 4.

2.2. Evaluation of the Synthesized 2-Amino-4-aryl-6-substituted Pyridine-3,5-dicarbonitrile as Corrosion Inhibitors. Alloys are exceedingly applied in manufacture processing applications and might undergo various acidic mediums. Acids were aggressive on the metal surface and progress to serious corrosion issues. Corrosion has been controlled by employing natural or synthetic inhibitors. Most of the utilizing inhibitors were from organic molecules with heteroatoms such as nitrogen, sulphur, phosphorus, and oxygen in addition to double bonds or aromatic rings in their structure that adsorbed on the surface of the metals. Corrosion inhibitors usually have the ability to control the corrosion through forming different kinds of films in various routes, such as adsorption through formation of precipitates or through forming of the inactive layer on the surface of the metal. Several organic inhibitors impeded the corrosion process by forming the invisible thin film on the metal surface.

The corrosion inhibition tendency of the synthesized 2-amino-3,5-dicyano-4-aryl-6-substituted aminopyridine derivatives was tested by studying the weight loss of steel coupons immersed in a solution of 6 M HCl for nine daytime intervals of immersion at room temperature. The weight loss (gravimetric method) is known to be the most widely used method of monitoring inhibition efficiency. The results of weight loss of steel coupons with the addition of different concentrations 200, 400, and 800 ppm of different inhibitors during 1, 3, 5, 7, and 9 days of immersion in 6 M HCl are

SCHEME 1

SCHEME 2

SCHEME 3

showed in Table 2 [28–31]. The corrosion rate (k), the inhibition efficiencies (η_w), and the degree of surface coverage (θ) were calculated from the following equations:

$$\theta = \frac{(W_o - W)}{W_o} \quad (1)$$

$$\eta_w = \left(\frac{(W_o - W)}{W_o} \right) \times 100, \quad (2)$$

$$k = \frac{W}{St}, \quad (3)$$

where S is the total area of the specimen, t is the immersion time, and W_o and W are the values of the weight loss in the absence and/or presence of different concentrations of the inhibitors. Data in Table 2 and Figures 1–3 show that the

synthesized 2-amino-3,5-dicyano-4-aryl-6-substituted aminopyridine derivatives **1**, **5**, **6**, and **8** protected steel from corrosion. The weight loss decreases, and inhibition efficiency increases in the presence of inhibitors. As a result of weight loss of mild steel in 6M HCl with and without addition of various concentration of 2-amino-3,5-dicyano-4-aryl-6-substituted aminopyridine derivatives. The efficiency increase with increasing the concentration of the inhibitor, which elucidated that the number of molecules adsorbed increased over the steel, blocking the active sites from acid and protecting the steel from corrosion. At 800 ppm which is the highest concentration, also, the best inhibition achievement of the derivative **5** was impute to presence of two methoxy groups attached to the phenyl. These electron groups increase the resonance capability toward conjugations owing to the presence of unshared electron pairs on the

SCHEME 4

nitrogen and oxygen atoms and thus increase the inhibition performance.

3. Experimental Section

All melting points measured on a Gallenkamp electric melting point apparatus are uncorrected. The infrared spectra were recorded in potassium bromide disks on a pye Unicam SP-3-300 and Shimadzu FT IR 8101 PC infrared spectrophotometers at the central laboratory of faculty of science, Ain Shams University.

The ^1H -NMR spectra were recorded on a Varian Mercury VX-300 MHz, using TMS as an internal standard in

deuterated dimethylsulphoxide (DMSO-d_6). Chemical shifts are measured in ppm. The mass spectra were recorded on a Shimadzu GCMS-QP-1000EX mass spectrometer At 70 eV, elemental analyses were carried out at the microanalytical center of Ain Shams University. All the reactions and the purity of the new compounds were monitored by TLC using TLC aluminum sheets silica gel F_{254} .

3.1. Chemistry. General method for synthesis of 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitriles **1–20** is as follows:

(a) One-pot multicomponent reactions by fusion

TABLE 2: Corrosion rate, surface covering, and corrosion inhibition efficiency of 1, 5, 6, and 8 inhibitors at room temperature.

No.	Dose (ppm)	1 day			3 days			5 days			7 days			9 days		
		K (mg·cm ⁻² ·h ⁻¹)	θ	η (%)	K (mg·cm ⁻² ·h ⁻¹)	θ	η (%)	K (mg·cm ⁻² ·h ⁻¹)	θ	η (%)	K (mg·cm ⁻² ·h ⁻¹)	θ	η (%)	K (mg·cm ⁻² ·h ⁻¹)	θ	η (%)
1	Blank	0.001590	—	—	0.001404	—	—	0.001484	—	—	0.00171	—	—	0.001968	—	—
	200	0.001267	0.203	20.3	0.001029	0.2665	26.65	0.001046	0.2949	29.49	0.00116	0.3168	31.68	0.001202	0.3891	38.91
	400	0.001059	0.3337	33.37	0.000876	0.3755	37.55	0.000886	0.4027	40.27	0.000911	0.4673	46.73	0.000922	0.5316	53.16
	800	0.00090	0.4321	43.21	0.000750	0.4657	46.57	0.000732	0.5068	50.68	0.000705	0.5874	58.74	0.000704	0.6421	64.21
5	200	0.001057	0.3350	33.50	0.000832	0.4072	40.72	0.000842	0.4327	43.27	0.000873	0.4892	48.92	0.000850	0.5678	56.78
	400	0.001010	0.3642	36.42	0.000794	0.4341	43.41	0.000795	0.4642	46.42	0.000839	0.5089	50.89	0.000806	0.5902	59.02
	800	0.000832	0.4767	47.67	0.000617	0.5601	56.01	0.000607	0.5910	59.10	0.000582	0.6594	65.94	0.000569	0.7104	71.04
6	200	0.001148	0.2779	27.79	0.000983	0.2997	29.97	0.001000	0.3261	32.61	0.001100	0.3564	35.64	0.001097	0.4423	44.23
	400	0.001021	0.3576	35.76	0.000801	0.429	42.9	0.000793	0.4654	46.54	0.000895	0.4762	47.62	0.000911	0.5369	53.69
	800	0.000939	0.4092	40.92	0.000781	0.4432	44.32	0.000752	0.4929	49.29	0.000735	0.5697	56.97	0.000748	0.6199	61.99
8	200	0.001149	0.2772	27.72	0.000979	0.3021	30.21	0.001021	0.3120	31.20	0.001153	0.3254	32.54	0.001169	0.4060	40.60
	400	0.00104	0.3415	34.15	0.000800	0.4296	42.96	0.000776	0.4771	47.71	0.000846	0.5048	50.48	0.000871	0.5573	55.73
	800	0.000940	0.4083	40.83	0.000767	0.4532	45.32	0.000686	0.5374	53.74	0.000653	0.6181	61.81	0.000654	0.6675	66.74

FIGURE 1: Relation between inhibition efficiency of aminopyridine derivatives in 6 M HCl and time at room temperature at 200 ppm.

FIGURE 2: Relation between inhibition efficiency of aminopyridine derivatives in 6 M HCl and time at room temperature at 400 ppm.

In a round bottom flask, aromatic aldehydes (0.01 mol), malononitrile (0.02 mol), and different primary amines (0.01 mol) were fused in sand bath for 3 h at 140–200°C. After cooling, the products were recrystallized from the proper solvent to give **1–20**.

(b) One-pot multicomponent reactions using AlCl_3 , ZnCl_2 , and/or FeCl_3 as a catalyst

Mixture of aromatic aldehydes (0.01 mol), malononitrile (0.02 mol), primary amines (0.03 mol), and catalyst (0.015 mol) was refluxed in ethanol (20 mL) for 6 h. The reaction mixture was poured onto ice/water, and the separated products were washed, dried, and recrystallized from the proper solvent to afford compounds (**1–20**).

3.1.1. 2-Amino-4-phenyl-6-(phenylamino)pyridine-3,5-dicarbonitrile (1). Yield (90%); yellow powder; m. p. 250–252°C (ethanol). FT-IR (KBr) (cm^{-1}) 3314, 3225 (NH_2), 3155

FIGURE 3: Relation between inhibition efficiency of aminopyridine derivatives in 6 M HCl and time at room temperature at 800 ppm.

(NH), 2208 (CN), and 1630 ($\text{C}=\text{N}$). $^1\text{H-NMR}$ (DMSO-d_6) δ (ppm) 9.10 (br.s, 1H, NH, D_2O exchangeable), 7.64 (br.s, 2H, NH_2 , D_2O exchangeable), and 7.56–7.05 (m, 10H, ArH). MS, m/z : (311). Anal. calcd for $\text{C}_{19}\text{H}_{13}\text{N}_5$ (311): C, 73.30; H, 4.21; and N, 22.49. Found: C, 73.36; H, 4.17; and N, 22.52.

3.1.2. 2-Amino-4-phenyl-6-(p-tolylamino)pyridine-3,5-dicarbonitrile (2). Yield (91%); yellow powder; m. p. 258–260°C (ethanol). FT-IR (KBr) (cm^{-1}) 3310, 3215 (NH_2), 3158 (NH), 2208 (CN), and 1630 ($\text{C}=\text{N}$). $^1\text{H-NMR}$ (DMSO-d_6) δ (ppm) 9.02 (br.s, 1H, NH, D_2O exchangeable), 7.54–7.09 (m, 9H, ArH), 7.49 (br.s, 2H, NH_2 , D_2O exchangeable), and 2.26 (s, 3H, CH_3). MS, m/z : (325). Anal. calcd for $\text{C}_{20}\text{H}_{15}\text{N}_5$ (325): C, 73.83; H, 4.65; and N, 21.52. Found: C, 73.88; H, 4.60; and N, 21.48.

3.1.3. 2,6-Diamino-4-phenylpyridine-3,5-dicarbonitrile (3). Yield (93%); yellow powder; m. p. 292–293°C (ethanol). FT-IR (KBr) (cm^{-1}) 3424, 3363 (NH_2), 3218, 3155 (NH_2), 2206 (CN), and 1623 ($\text{C}=\text{N}$). $^1\text{H-NMR}$ (DMSO-d_6) δ (ppm): 7.52–7.43 (m, 5H, ArH) and 7.23 (br.s, 4H, NH_2 , D_2O exchangeable). MS, m/z : (235). Anal. calcd for $\text{C}_{13}\text{H}_5\text{N}_5$ (235): C, 66.37; H, 3.86; and N, 29.77. Found: C, 66.41; H, 3.81; and N, 29.71.

3.1.4. 2-Amino-6-(ethylamino)-4-phenylpyridine-3,5-dicarbonitrile (4). Yield (95%); yellow powder; m. p. 226–228°C (ethanol). FT-IR (KBr) (cm^{-1}) 3323, 3218 (NH_2), 3168 (NH), 2225 (CN), and 1623 ($\text{C}=\text{N}$). $^1\text{H-NMR}$ (DMSO-d_6) δ (ppm) 7.92 (br.s, 1H, NH, D_2O exchangeable), 7.54–7.43 (m, 5H, ArH), 7.23 (br.s, 2H, NH_2 , D_2O exchangeable), 3.32 (q, 2H, CH_2), and 1.10 (t, 3H, CH_3). MS, m/z : (263). Anal. calcd for $\text{C}_{15}\text{H}_{13}\text{N}_5$ (263): C, 68.42; H, 4.98; and N, 26.60. Found: C, 68.47; H, 4.92; and N, 26.56.

3.1.5. 2-Amino-4-(4-methoxyphenyl)-6-((4-methoxyphenyl)amino)pyridine-3,5-dicarbonitrile (**5**). Yield (89%); brown powder; m. p. 256–258°C (acetone). FT-IR (KBr) (cm^{-1}) 3299, 3199 (NH_2), 3124 (NH), 2209 (CN), and 1606 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 9.17 (br.s, 1H, NH, D_2O exchangeable), 7.49–6.76 (m, 8H, ArH), 4.32 (br.s, 2H, NH_2 , D_2O exchangeable), 3.86 (s, 3H, OCH_3), and 3.83 (s, 3H, OCH_3). MS, m/z : (371). Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{N}_5\text{O}_2$ (371): C, 67.91; H, 4.61; and N, 18.86. Found: C, 67.95; H, 4.55; and N, 18.81.

3.1.6. 2-Amino-4-(4-methoxyphenyl)-6-(*p*-tolylamino)pyridine-3,5-dicarbonitrile (**6**). Yield (87%); brown powder; m. p. 268–270°C (acetone). FT-IR (KBr) (cm^{-1}) 3304, 3202 (NH_2), 3128 (NH), 2211 (CN), and 1607 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 9.10 (br.s, 1H, NH, D_2O exchangeable), 7.52–7.02 (m, 8H, ArH), 6.89 (br.s, 2H, NH_2 , D_2O exchangeable), 3.88 (s, 3H, OCH_3), and 2.30 (s, 3H, CH_3). MS, m/z : (355). Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{N}_5\text{O}$ (355): C, 70.97; H, 4.82; and N, 19.71. Found: C, 71.04; H, 4.78; and N, 19.66.

3.1.7. 4-((6-Amino-3,5-dicyano-4-(4-methoxyphenyl)pyridin-2-yl)amino)benzoic Acid (**7**). Yield (82%); brown powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) broad band centered at 3326 (OH, NH_2), 3195 (NH), 2212 (CN), 1732 ($\text{C}=\text{O}$), and 1630 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 10.40 (br.s, 1H, OH, D_2O exchangeable), 9.10 (br.s, 1H, NH, D_2O exchangeable), 8.06–7.18 (m, 8H, ArH), 6.67 (br.s, 2H, NH_2 , D_2O exchangeable), and 3.89 (s, 3H, OCH_3). MS, m/z : (385). Anal. calcd for $\text{C}_{21}\text{H}_{15}\text{N}_5\text{O}_3$ (385): C, 65.45; H, 3.92; and N, 18.17. Found: C, 65.49; H, 3.87; and N, 18.13.

3.1.8. 2-((6-Amino-3,5-dicyano-4-(4-methoxyphenyl)pyridin-2-yl)amino)benzoic Acid (**8**). Yield (79%); brown powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) broad band centered at 3341 (OH, NH_2), 3219 (NH), 2208 (CN), 1735 ($\text{C}=\text{O}$), and 1630 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 11.04 (br.s, 1H, OH, D_2O exchangeable), 9.99 (br.s, 1H, NH, D_2O exchangeable), 7.76–7.07 (m, 8H, ArH), 3.85 (s, 3H, OCH_3), and 6.97 (br.s, 2H, NH_2 , D_2O exchangeable). MS, m/z : (385). Anal. calcd for $\text{C}_{21}\text{H}_{15}\text{N}_5\text{O}_3$ (385): C, 65.45; H, 3.92; and N, 18.17. Found: C, 65.50; H, 3.96; and N, 18.21.

3.1.9. 2-Amino-6-((2-hydroxyphenyl)amino)-4-(4-methoxyphenyl)pyridine-3,5-dicarbonitrile (**9**). Yield (84%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) 3424 (OH), 3373, 3286 (NH_2), 3219 (NH), 2206 (CN), and 1630 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 10.08 (br.s, 1H, OH, D_2O exchangeable), 9.94 (br.s, 1H, NH, D_2O exchangeable), 6.85–7.71 (m, 8H, ArH), 6.83 (br.s, 2H, NH_2 , D_2O exchangeable), and 3.81 (s, 3H, OCH_3). MS, m/z : (357). Anal. calcd for $\text{C}_{20}\text{H}_{15}\text{N}_5\text{O}_2$ (357): C, 67.22; H, 4.23; and N, 19.60. Found: C, 67.28; H, 4.18; and N, 19.56.

3.1.10. 2-((4-Acetylphenyl)amino)-6-amino-4-(4-methoxyphenyl)pyridine-3,5-dicarbonitrile (**10**). Yield (76%); brown powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) 3326, 3232 (NH_2), 3195 (NH), 2209 (CN), 1698 (CO), and 1630 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 9.93 (br.s, 1H, NH, D_2O exchangeable), 7.89–7.02 (m, 8H, ArH), 6.89 (br.s, 2H, NH_2 , D_2O exchangeable), 3.83 (s, 3H, $-\text{OCH}_3$), and 2.53 (s, 3H, CH_3). MS, m/z : (383). Anal. calcd for $\text{C}_{22}\text{H}_{17}\text{N}_5\text{O}_2$ (383): C, 68.92; H, 4.47; and N, 18.27. Found: C, 68.97; H, 4.43; and N, 18.21.

3.1.11. 2-Amino-4-(4-chlorophenyl)-6-(phenylamino)pyridine-3,5-dicarbonitrile (**11**). Yield (91%); brown powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) 3416, 3303 (NH_2), 3215 (NH), 2209 (CN), and 1621 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 9.93 (br.s, 1H, NH, D_2O exchangeable), 7.78–7.02 (m, 9H, ArH), and 6.89 (br.s, 2H, NH_2 , D_2O exchangeable). MS, m/z : (345). Anal. calcd for $\text{C}_{19}\text{H}_{12}\text{ClN}_5$ (345): C, 66.00; H, 3.50; and N, 20.25. Found: C, 66.04; H, 3.46; and N, 20.21.

3.1.12. 2-Amino-4-(4-chlorophenyl)-6-(4-methoxyphenyl)amino)pyridine-3,5-dicarbonitrile (**12**). Yield (92%); brown powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) 3325, 3222 (NH_2), 3158 (NH), 2207 (CN), and 1629 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 9.19 (br.s, 1H, NH, D_2O exchangeable), 7.65–6.79 (m, 8H, ArH), 6.92 (br.s, 2H, NH_2 , D_2O exchangeable), and 3.83 (s, 3H, OCH_3). MS, m/z : (375). Anal. calcd for $\text{C}_{20}\text{H}_{14}\text{ClN}_5\text{O}$ (375.1): C, 63.92; H, 3.76; and N, 18.64. Found: C, 63.98; H, 3.71; and N, 18.58.

3.1.13. 2-Amino-4-(4-chlorophenyl)-6-((4-nitrophenyl)amino)pyridine-3,5-dicarbonitrile (**13**). Yield (88%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) 3322, 3227 (NH_2), 3128 (NH), 2209 (CN), and 1623 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 9.10 (br.s, 1H, NH, D_2O exchangeable), 8.01–7.06 (m, 8H, ArH), and 7.78 (br.s, 2H, NH_2 , D_2O exchangeable). MS, m/z : (390). Anal. calcd for $\text{C}_{19}\text{H}_{11}\text{ClN}_6\text{O}_2$ (390): C, 58.40; H, 2.84; and N, 21.51. Found: C, 58.35; H, 2.79; and N, 21.45.

3.1.14. 2-Amino-4-(4-chlorophenyl)-6-(*p*-tolylamino)pyridine-3,5-dicarbonitrile (**14**). Yield (90%); yellow powder; m. p. over 200–202°C (acetone). FT-IR (KBr) (cm^{-1}) 3285, 3238 (NH_2), 3137 (NH), 2207 (CN), and 1613 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 7.45 (br.s, 1H, NH, D_2O exchangeable), 6.82–6.40 (m, 8H, ArH), 4.65 (br.s, 2H, NH_2 , D_2O exchangeable), and 2.30 (s, 3H, CH_3). MS, m/z : (359). Anal. calcd for $\text{C}_{20}\text{H}_{14}\text{ClN}_5$ (359): C, 66.76; H, 3.92; and N, 19.46. Found: C, 66.71; H, 3.97; and N, 19.53.

3.1.15. 2-Amino-6-(phenylamino)-4-styrylpyridine-3,5-dicarbonitrile (**15**). Yield (78%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm^{-1}) 3372, 3265 (NH_2), 3160 (NH), 2202 (CN), and 1626 ($\text{C}=\text{N}$). ^1H -NMR ($\text{DMSO}-d_6$) δ (ppm) 10.13 (br.s, 1H, NH, D_2O exchangeable), 7.50–6.97 (m, 10H,

ArH), 7.24 (d, 1H, =CH), 6.99 (d, 1H, =CH), and 6.95 (br.s, 2H, NH₂, D₂O exchangeable). MS, *m/z*: (337). Anal. calcd for C₂₁H₁₅N₅ (337): C, 74.76; H, 4.48; and N, 20.76. Found: C, 74.72; H, 4.52; and N, 20.81.

3.1.16. 2-Amino-6-((4-methoxyphenyl)amino)-4-styrylpyridine-3,5-dicarbonitrile (16). Yield (81%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm⁻¹) 3354, 3207 (NH₂), 3118 (NH), 2206 (CN), and 1613 (C=N). ¹H-NMR (DMSO-d₆) δ (ppm) 10.13 (br.s, 1H, NH, D₂O exchangeable), 7.63–7.04 (m, 9H, ArH), 7.24 (d, 1H, =CH), 6.99 (d, 1H, =CH), 6.95 (br.s, 2H, NH₂, D₂O exchangeable), and 3.83 (s, 3H, OCH₃). MS, *m/z*: (367). Anal. calcd for C₂₂H₁₇N₅O (367): C, 71.92; H, 4.66; and N, 19.06. Found: C, 71.98; H, 4.61; and N, 18.98.

3.1.17. 2-Amino-6-((4-nitrophenyl)amino)-4-styrylpyridine-3,5-dicarbonitrile (17). Yield (73%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm⁻¹) 3344, 3215 (NH₂), 3120 (NH), 2203 (CN), and 1606 (C=N). ¹H-NMR (DMSO-d₆) δ (ppm) 10.13 (br.s, 1H, NH, D₂O exchangeable), 6.89 (br.s, 2H, NH₂, D₂O exchangeable), 7.63–7.04 (m, 9H, ArH), 7.21 (d, 1H, =CH), and 6.96 (d, 1H, =CH). MS, *m/z*: (382). Anal. calcd for C₂₁H₁₄N₆O₂ (382): C, 65.96; H, 3.69; and N, 21.98. Found: C, 65.91; H, 3.74; and N, 22.03.

3.1.18. 2-Amino-6-(ethylamino)-4-styrylpyridine-3,5-dicarbonitrile (18). Yield (88%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm⁻¹) broad band at 3346 (NH₂, NH), 2203 (CN), and 1614 (C=N). ¹H-NMR (DMSO-d₆) δ (ppm) 7.86–7.36 (m, 5H, ArH), 7.80 (br.s, 1H, NH, D₂O exchangeable), 7.25 (d, 1H, =CH), 6.77 (br.s, 2H, NH₂, D₂O exchangeable), 6.46 (d, 1H, =CH), 3.64 (q, 2H, CH₂), and 1.10 (t, 3H, CH₃). MS, *m/z*: (289). Anal. calcd for C₁₇H₁₅N₅ (289): C, 70.57; H, 5.23; and N, 24.20. Found: C, 70.53; H, 5.29; and N, 24.25.

3.1.19. 2-Amino-6-(benzylamino)-4-styrylpyridine-3,5-dicarbonitrile (19). Yield (84%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm⁻¹) 3364, 3262 (NH₂), 3060 (NH), 2203 (CN), and 1612 (C=N). ¹H-NMR (DMSO-d₆) δ (ppm) 8.83 (br.s, 1H, NH, D₂O exchangeable), 4.15 (s, 2H, NHCH₂), 6.89 (br.s, 2H, NH₂, D₂O exchangeable), 7.60–7.44 (m, 10H, ArH), 7.20 (d, 1H, =CH), and 6.93 (d, 1H, =CH). MS, *m/z*: (351). Anal. calcd for C₂₂H₁₇N₅ (351): C, 75.19; H, 4.88; and N, 19.93. Found: C, 75.26; H, 4.82; and N, 19.86.

3.1.20. 2-Amino-6-((2-hydroxyethyl)amino)-4-styrylpyridine-3,5-dicarbonitrile (20). Yield (82%); black powder; m. p. over 300°C (acetone). FT-IR (KBr) (cm⁻¹) broad band centered at 3335 (OH, NH₂, NH), 2207 (CN), and 1623 (C=N). ¹H-NMR (DMSO-d₆) δ (ppm) 8.83 (br.s, 1H, NH, D₂O exchangeable), 7.60–7.30 (m, 5H, ArH), 7.20 (d, 1H, =CH), 6.93 (d, 1H, =CH), 6.89 (br.s, 2H, NH₂, D₂O exchangeable), 4.55 (br.s, 1H, OH, D₂O exchangeable), 3.60 (t, 2H, CH₂CH₂OH), and 3.15 (t, 2H, NHCH₂CH₂). MS, *m/z*:

(305). Anal. calcd for C₁₇H₁₅N₅O (305): C, 66.87; H, 4.95; and N, 22.94. Found: C, 66.97; H, 4.89; and N, 22.86.

3.2. Experimental for Corrosion. Coupons of steel were cut into 1 × 1 × 0.5 cm³ dimensions are used for the gravimetric method. The specimens are washed, dried, and weighted. Then, coupons were immersed in a beaker containing 50 ml of a solution of 6 M HCl for 9 days with different concentrations of the synthesized 2-amino-3,5-dicyano-4-aryl-6-substituted aminopyridine derivatives. The specimens were washed, dried, and reweighted to take the difference in weight of steel coupons with and without the inhibitors, corrosion rate (CR), inhibition efficiencies (η (%)), and the degree of surface coverage (θ) for different concentrations at room temperature.

4. Conclusion

In summary, we have developed for the first time one-pot multicomponent reaction under the fusion condition without using solvent and catalysts. With this method, a wide range of novel 2-amino-3,5-dicyano-4-aryl-6-substituted aminopyridine derivatives were synthesized in high yields with a board substrate of functional groups. The synthesized pyridine derivatives act as corrosion inhibitors, and the rate of inhibition efficiency increases with the increasing concentration of the inhibitor.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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